Highly selective liquid-phase oxidation of cyclohexane to KA oil over Ti-MWW catalyst: evidence of formation of oxyl radicals

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Introduction

Cyclohexanol and cyclohexanone (the mixture is known as KA oil, production >200 ktn/year) are readily oxidized to adipic acid, an important intermediate in the manufacture of condensation polymers, in particular polyamides such as Nylon 6.6.[1] KA oil is industrially produced at Solvay facilities by the partial oxidation of cyclohexane in a process involving two consecutive steps: (1) noncatalytic autoxidation of cyclohexane by oxygen to cyclohexyl hydroperoxide (CHHP), and (2) deperoxidation of CHHP to KA oil using homogeneous and environmentally unfriendly Co(II) or Cr(VI) catalysts.

Aiming to improve the environmental footprint and the economics of Nylon production, we present here a novel and green catalyst, i.e. Ti-MWW, for partial cyclohexane oxidation.[2] The catalytic performance was compared to TS-1, Ti-BEA and Ti-MOR zeolites, all three considered as benchmarks. The effect of the reaction temperature, time, catalyst amount and catalytic stability of Ti-MWW has been explored in detail. The location of the active sites was investigated by selective poisoning of the active sites. Electron paramagnetic resonance (EPR) experiments were combined with DFT calculations to study the reaction mechanism and gain insight into the nature of the active species during cyclohexane oxidation.

Materials and Methods

Four different Ti-containing zeolites with different effective channel sizes were selected to assess possible shape selectivity effects for cyclohexane oxidation: TS-1 (5.3 Å), Ti-MWW (5.3 Å, 7.0 Å), Ti-MOR (6.7 Å), and Ti-BEA (7.0 Å). Ti-MWW-1 (Si/Ti=49) was obtained commercially from Zhejiang TWRD New Materials Co., Ltd, China, while Ti-MWW-2 (Si/Ti=67), Ti-BEA (Si/Ti=63), TS-1 (Si/Ti=32), and Ti-MOR (Si/Ti=84) zeolites were prepared according to previous reports.[3]

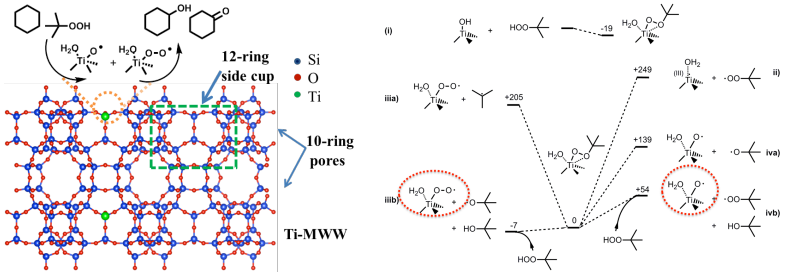
The catalytic tests were performed in a sealed tube under air at 30-80 °C using 0.1 g catalyst and a cyclohexane solution (4.0 g) containing t-butylhydroxyperoxide (TBHP, 7.7 wt.%). The analyses were carried out in a GC (Agilent 7820A) equipped with a DB-WAX column and a flame ionization detector. A wide series of techniques were used to assess the phase and textural properties of the different catalysts (XRD & BET), the bulk and surface Ti/Si molar ratios (ICP & XPS), the nature of the Ti species (UV-Vis), and the presence of radical intermediates (EPR, 118 K, 0.42 GHz, 20.25 mW). DFT simulations were performed on cage-like clusters as model Ti sites for Ti-MWW, at the B3LYP 6-311+G(d,p)//6-31G(d) level, using SPARTAN '10.1 for geometry optimization and energies, and ORCA 2.9.1 for obtaining the principal values of the EPR g-tensor.

Results and Discussion

Table 1 summarizes the catalytic properties of different Ti-containing zeolites tested in this study for the liquid-phase oxidation of cyclohexane using t-butyl hydroperoxide (TBHP, 7-8 wt.%) as model oxidant. Ti-MWW zeolite displayed the highest activity toward KA oil with an overall yield ca. 10% at 80 °C. Furthermore, Ti-MWW showed a stable performance and could be recycled at least 4 times without detectable Ti leaching and loss of structure stability. The active sites for cyclohexane oxidation appeared to be located near external 12-ring cups in the Ti-MWW framework as suggested by a series of position-selective poisoning tests with tripropyl- and triphenylamine, impelling cyclohexane diffusion within the internal 10-ring channels (Scheme 1 left).

Table 1. Physicochemical properties and cyclohexane oxidation results of various titanosilicate catalysts. Reaction conditions: 80 °C, 0.10 g catalyst, 4 g cyclohexane with 7.7 wt % TBHP.

Catalyst	Pore size (Å)	Si/Ti (XPS)	TBHP Conv. %	KA Sel. %	KA Yield%	A/K	Turnover number † (surface Ti)
Ti-MWW	5.3, 7.0	53	10.7	90.1	9.6	8.4	47.4
TS-1	5.3	33	10.1	28.5	2.9	1.0	4.8
Ti-BEA	6.7	52	42.4	17.6	7.5	∞	-
Ti-MOR	7.0	-	0.2	98.1	0.2	∞	-



Scheme 1. Graphic illustration of KA oil formation on 12-ring side cups of Ti-MWW (left). Formation of Ti-(η^2-OOtBu)(H_2O). ii-iv) Formation of potential radical intermediates via uni- and bimolecular cleavage of Ti-η^1(OOtBu)(H_2O) (right).

EPR experiments supported by DFT calculations suggest the coexistence of both Ti(IV)-OO• (peroxyl) and Ti(IV)-O• (oxyl) species generated through bimolecular pathways, implying simultaneously $(SiO)_3Ti(OOtBu)$ species and tBuOOH(Scheme 1 right). Notably, this is the first time that oxyl species have been detected particularly with the help of DFT calculations. Predicted differences of g tensors between peroxyl and oxyl species at various hydration levels in the presence of cyclohexane were consistent with the EPR spectra.

References

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